

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an information-recording medium and, in particular, to an information-recording medium utilizing a stable change in specific charge-transport properties of a liquid crystal material.

[0002]

[Prior Art]

In recent years, various information-recording media, such as magnetic recording media, thermal recording media and optical recording media, have been developed and put to practical use. The present inventors have hitherto made studies on optical, physico-chemical or electric characteristics of liquid crystal materials and, up to now, have proposed a liquid crystal charge-transport material in which charge-transport properties of a specific liquid crystal system is focused on (for example, Japanese Patent Application No. 76820/1998).

[0003]

[Problems to be Solved by the Invention]

The present invention has been made as a result of attention to a property of such a liquid crystal material that the charge-transport properties of the liquid crystal material stably vary upon phase transfer between a plurality of liquid crystal phases, and it is an object of the present invention to provide a novel information-recording medium that records information upon application of thermal energy and reads the recorded information with detection of the photoelectric current generated by light applied to an information-recorded portion and, in addition, can realize multi-valued information-recording or analog information-recording.

[0004]

[Means for Solving the Problems]

In order to attain the above-mentioned object, the information-recording medium according to the present invention is characterized to comprise: a pair of electrodes; and a liquid crystal material filled into a gap between the said electrodes, the said liquid

crystal material having such a property that charge-transport properties vary according to a phase transfer between a plurality of stable liquid crystal phases of the liquid crystal or (and) a history of the phase transfer.

[0005]

According to the present invention, the phase transfer of the above-mentioned liquid crystal material occurs upon a change in temperature of the said liquid crystal material. This phase transfer is reversible, and the domain structure of each liquid crystal phase that varied is stable.

[0006]

Further, according to the information-recording medium of the present invention, information may be recorded with thermal energy applied, and the recorded information may be read with measurement of the value of a photoelectric current generated by light applied to an information-recording portion.

[0007]

Thus, the information-recording medium of the present invention skillfully utilizes phase transfer between a plurality of stable liquid crystal phases of a liquid crystal material or (and) such a property that the charge-transport properties are changed according to the history of the phase transfer. By virtue of this constitution, despite the fact that the liquid crystal material layer has a single layer structure, it is possible to realize information-recording that relies upon a phase change as a result of phase transfer between two or more liquid crystal phases and information-recording depending upon the level of thermal energy. Therefore, not only binary digital information but also multi-valued information or analog information may be recorded.

[0008]

Further, according to the present invention, mere filling of a liquid crystal material into a specific gap between electrodes can provide a medium or an element. Therefore, the present invention is also advantageous in that the information-recording medium can be simply produced.

[0009]

[Forms to Implement the Invention]

The information-recording medium according to the present invention, as Fig. 1 shows one embodiment thereof, comprises: a pair of substrates 1a and 1b; electrodes 2a and 2b provided respectively on the substrates; spacers 4 provided between the electrodes to form a gap; and a liquid crystal material 3 filled into the gap. This liquid crystal material has such a property that the charge-transport properties of the liquid crystal material vary according to phase transfer of the liquid crystal material between a plurality of stable liquid crystal phases.

[0010]

Preferably, at least one of the substrates 1a and 1b is formed of a light-transparent material, such as glass, although the material is not particularly limited. Electrodes provided on the substrates are preferably transparent electrodes of ITO (Indium Tin Oxide) or the like. The pair of substrates for constituting cells of the information-recording medium are integrated with each other through the spacers 4 with the aid of fixing means, such as an adhesive, and a liquid crystal material is filled into the gap created between the substrates.

[0011]

The liquid crystal material is preferably a bipolar photoconductive liquid crystal, and specific examples of preferred liquid crystal materials usable herein include rod-like liquid crystal systems, for example, phenylnaphthalene liquid crystals, such as 2-(4'-octylphenyl)-6-dodecyloxynaphthalene (abbreviated to "8-PNP-012"), 2-(4'-octylphenyl)-6-butyloxynaphthalene (abbreviated to "8-PNP-04"), and 10-PNP-09, and biphenyl liquid crystals, such as 2-4'-heptyloxy-4'-octylbiphenyl (abbreviated to "60-BP-8").

[0012]

Further, monopolar photoconductive liquid crystals may also be preferably used as far as the polarity of the voltage applied to electrodes, to which excitation light is applied, is selected. Specific examples of preferred monopolar photoconductive liquid crystals usable herein include phenylbenzothiazole liquid crystals, for example, biphenyl liquid

crystals having carbonyl and alkoxy in their ends, such as 2-(4'-heptyloxyphenyl)-6-dodecylthiobenzothiazole (abbreviated to "70-PBT-S12"), 4-heptyloxy-4'-dodecylbiphenyl (abbreviated to "70-BP-CO-11"), and 4-hexyloxy-4'-butanoylbiphenyl (abbreviated to "60-BP-CO-4").

[0013]

For example, the above-mentioned 8-PNP-012 exhibits a phase transfer behavior of Cryst. -79°C-SmB-101°C-SmA-121°C-Iso. In the SmB phase on low temperature side, for both electrons and holes, the mobility is  $1.6 \times 10^{-3} \text{ cm}^2/\text{Vs}$ , and, also in the SmA phase on high temperature side, the mobility is  $2.5 \times 10^{-4} \text{ cm}^2/\text{Vs}$ .

[0014]

Interestingly, the above-mentioned specific liquid crystal material has such a property that the charge-transport properties vary according to phase transfer caused by a change in temperature between two or more stable liquid phases. Here, what is more important is as follows. In the conventional liquid crystal phase, polycrystalline structural defects behave as traps, leading to significant inhibition of charge-transport properties, whereas, according to the present invention, the specific polydomain structure of the liquid crystal phase formed does not inhibit the charge-transport properties.

[0015]

It is necessary to note that the above unexpected advantageous properties can be more effectively developed with the relationship controlled between the thickness of the gap between the electrodes and the domain size in the initial state of the liquid crystal material so as to satisfy a specific requirement.

[0016]

Specifically, according to a preferred embodiment of the present invention, the size of the gap between the electrodes is larger than the domain size at least in the initial state of the liquid crystal material. More specifically, the thickness between the pair of electrodes preferably satisfies both requirements represented by inequalities (A) and (B):

(Permeation depth at excitation light wavelength of liquid crystal material) < (Thickness between pair of electrodes) (A)

(Thickness between pair of electrodes) < (Thickness capable of exhibiting field

strength so as to enable reading of photoelectric current) (B)

[0017]

For example, when the above-mentioned 8-PNP-012 is used as the liquid crystal material, the distance between the electrodes is suitably in the range 1.5 to 150  $\mu\text{m}$ , more preferably 5.0 to 50.0  $\mu\text{m}$ .

[0018]

According to the present invention, the phase transfer of the above-mentioned liquid crystal material occurs upon a change in temperature of the liquid crystal material. More specifically, phase transfer or a change in domain structure attributable to the phase transfer can be created with thermal energy application means, such as a thermal head or a laser beam. Further, the use of the thermal energy application means can realize high-density information recording.

[0019]

For example, in the information-recording medium shown in Fig. 1, upon application of a laser beam from any side of the substrate, thermal energy is supplied to the whole area of the cell or a part thereof. This creates phase transfer or a change in domain structure attributable to the phase transfer according to the thermal energy applied to the liquid crystal material layer. The charge-transport properties vary according to the transferred phase. The domain structure in the transferred phase is stable unless thermal energy on such a level as to cause transfer to the isotropic phase is applied to the same site. Thus, inherent information can be recorded.

[0020]

On the other hand, the magnitude of photoelectric current attributable to charges, which have been injected with the application of light (for example, pulsed light as a trigger) into the information-recorded portion, is determined by the charge-transport properties in the light-applied site. Therefore, the recorded information can be read with the quantity detected as a current value from the electrode.

[0021]

Further, in the information recording, varying the level of thermal energy applied to thereby develop charge-transport properties between those of two phases

according to the energy level can realize binary digital information recording, as well as multi-valued or analog information recording.

[0022]

Moreover, according to the present invention, the background for information recording may be in such a state that the charge-transport properties are inhibited attributable to polycrystalline structural defects in the initial state of the liquid crystal charge-transport material and, in this case, the information recording may be carried out with phase transfer caused in the background upon application of thermal energy.

[0023]

[Examples]

Hereinafter, the following production example further illustrates the present invention.

#### Production Example

Glass substrates provided with ITO were disposed as transparent electrodes so as to face each other while a gap of 150  $\mu\text{m}$  is provided between the electrodes through a polyimide sheet as a spacer. The spacing between both of the substrates was fixed by means of a thermoset resin to form a sandwich cell. A liquid crystalline charge-transport material (8-PNP-012) in the form of an isotropic phase (150°C) was poured into the cell with capillarity. In this liquid crystal material, molecule aligning treatment, which is usually required, is not particularly necessary, as the liquid crystal material has such a property that the material molecules used in its major axis direction are aligned horizontally to the glass substrate. This property is utilized in the present production example.

[0024]

At a cooling rate at 10°C/min or lower, in general, upon formation of the smectic phase structure molecules of the liquid crystal material composed of rod-like molecules including 8-PNP-012 are likely to arrange so that the substrate is horizontal to the major axis. In the smectic A phase, since there is no anisotropy around the major axis, phase transfer at the time of cooling leads to a tendency that the layer structure is isotropically grown in the thicknesswise direction of the cell and in the direction parallel to the substrate. When the major axis direction of molecules is not regulated in a

specific direction with the control of the orientation, the major axis direction of molecules within growth nuclei (domain source) of phase structures, which have been simultaneously developed in many places, is random in an early stage. In this case, upon contact between small domains at the time of growth, a more stable domain absorbs the other domain. The growth continues in this way. Finally, even though adjacent domains have different alignment directions, a stable state is attained on the whole with the influence of a substrate wall surface or the like. In addition to the above phenomenon, unexpectedly, a phenomenon was observed, in which domain boundaries formed at that time do not inhibit the charge-transport properties. In general, the larger the cell gap becomes, the larger the domain size gets. However, it has been found that the charge-transport properties remain unchanged regardless of the domain size.

[0025]

Further, in the present example, it was found that, when the cell is sandwiched between two heat sinks formed of an aluminum plate, cooling of the liquid crystal material from an isotropic phase at such a rate as to reach the crystal phase (for about 5 sec), polydomain structures formed of domains having a size smaller than the size of the cell gap can be provided in all of the liquid crystal phases (SmA phase and SmB phase) which the liquid crystal material exhibits.

[0026]

Once the domain structure has been formed in the liquid crystal phase, the basic shape of the domain structure is stably maintained until the temperature is raised to create an isotropic phase again. In the present example, it is estimated that the rate of cooling for transfer from the isotropic phase to the liquid crystal phase is a major factor which determines whether or not fine domains can be stably present.

[0027]

The TOF (Time-of-Flight) method was used to measure the charge-transport properties of the cell, occupied by domains smaller than the cell gap, prepared according to the above procedure. In the TOF method, the time necessary for the carrier generated in the sample to travel to the counter electrode is investigated from a transient photoelectric current waveform obtained with the application of pulsed light, and the carrier mobility

is determined based on the results. In this case, pulsed light of a nitrogen laser (pulse width 600 psec, wavelength 337 nm, output 40  $\mu$ J) was used as the excitation light, and a direct voltage (maximum 500 V) was applied to the sample fixed onto a hot stage.

[0028]

As a result, it was found that the charge-transport property (carrier mobility) is provided at the time when an inflection point appears in the current value.

[0029]

Initial state: When the temperature is raised from room temperature (crystal phase) to a temperature at which the SmB phase is developed (90°C), any transient current indicating good charge-transport properties (about  $10^{-3}$  cm<sup>2</sup>/Vs) inherent in this material is not observed. This is considered attributable to the fact that the effect of allowing structural barriers, which significantly inhibit the charge-transport properties in the crystal phase, to remain upon phase transfer to a phase adjacent to the crystal phase has been emphasized with the size of the polydomain being made smaller than the cell gap. (This state is such that properties of a polycrystal have been substantially imparted in spite of the liquid crystal phase.) This state is called "off state" for the sake of convenience. (For some applications, this state may be regarded as "on state".)

[0030]

Rewriting (1): When the temperature of the whole cell in an off state was raised to a temperature at which the SmA phase appeared (110°C) followed by a temperature falling to return the phase to the SmB phase, a transient current reflecting the charge transportation in this material was observed. This is considered attributable to such a phenomenon that the polycrystalline charge-transport trap provided in the off state has disappeared with phase transfer once caused to a phase having low crystallinity.

[0031]

The same effect was attained when, in the cell face maintained in the SmB phase, a part of the electrode site was heated for 15 sec by means of a thermal head (in this case, the head temperature needs to be below the temperature 118°C at which transfer to the isotropic phase occurs; the head temperature in the present example being 110°C) followed by standing to return the temperature of the heated site to 90°C. It was demonstrated



that heating any place or region on the electrode permits the heated site to be rewritten into charge-transfer properties different from those of the sites in an off state.

[0032]

In this case, the rewriting does not necessarily need to be carried out in electrode region units. That is, even when any region within at least one pair of counter electrodes is selectively rewritten, the written information can be read in terms of the charge-transport properties and the current value, for example, with a read-out light selectively applied utilizing scanning irradiation.

[0033]

In addition to this, the application of a laser beam having a proper output to conduct heat treatment is possible as the rewriting means.

[0034]

Rewriting (2): When a cell in an off state or a region subjected to the above-writing was heated to a temperature (130°C) at which the isotropic phase appeared, followed by cooling to the SmB phase at a rate of 10°C/min, a region different from the off-state region was obtained, in which the domain size was larger than the cell gap. Both rewriting of the whole cell and selective rewriting of the domain size using a thermal head having a head temperature of 150°C were carried out. As a result, clearer rewriting of the charge-transport properties than the case of the rewriting (1) was able to be confirmed.

[0035]

In the above-mentioned rewriting (1), since the damping rate of the transient current waveform (which reflects the situation of trapping of the resultant carrier in the medium) is identical to that of the current waveform in the rewriting (2), good charge-transport properties were obtained. It is considered that, since photoexcitation for reading is scattered by fine domains, the injection of charges is unsatisfactory, resulting in small transient current values. The rewriting (2) corresponds to the case where an element limiting the charge injection in this cell construction was eliminated with the domain structure varying as a result of phase transfer to the isotropic phase.

[0036]

Further, for both of writing by means of a thermal head and writing by means

of a laser beam, the degree of the change in domain structure caused by the phase transfer can be regulated with the level of thermal energy continuously varying for writing. This can realize intermediate control in charge-transport properties and current values as output information.

[0037]

[Effect of the Invention]

As is obvious from the results of the above example, the present invention can provide a novel information-recording medium which records information upon application of thermal energy and reads the recorded information with detection of the value of photoelectric current generated by light applied to the information-recorded portion, and can realize multi-valued information recording or analog information recording.

[Brief Description of the Drawings]

[Fig. 1]

A cross-sectional view showing the construction of an information-recording medium according to one embodiment of the present invention.

[Explanation of numerals]

- 1a, 1b Substrate
- 2a, 2b Electrode
- 3 Liquid crystal material
- 4 Spacer